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Fiber optic methane sensor for mines*

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Different types of fiber optic methane sensor, especially for mining application, have been reviewed in this paper. Optical absorption and differential optical absorption techniques for the remote detection of methane gas using low-loss silica fiber have been discussed. Infrared fiber optic, sol-gel and correlation spectroscopy methods have been described in brief. Another noble technique based on attenuation of evanescent field has been enunciated using D-fiber. Merits and demerits of each technique and their suitability to mining industry have been highlighted. Optical fiber, being a dielectric, non-metallic and non-sparking, is an intrinsically safe medium and is ideally suited to the hazardous environment present in mines.

1. Introduction

Continuous monitoring of the methane gas in underground coal mines is very important for the safe and fearless operation of the mines. This is because methane-air-mixture is highly explosive between 5–14.5%. At present, methane is routinely monitored between 0–5% using catalytic combustion type methane sensor which is an electrically heated pellistor. In the latter, palladium is deposited on platinum wire which acts as catalyst for methane gas. In the case of hybrid thick-film technology, use of tin-oxide based methane sensors with improved sensitivity and reliability has been reported by several authors [1]–[7], but these are also based on heating effect of semiconductor oxides. Several other methods of detection of methane gas in underground mines have been described by different researchers in the recent mine safety conference papers [8]. Catalytic combustion type methane devices are not intrinsically safe and poisoning of the catalyst may occur in certain environments such as grease, transformer oil, electrical insulator, Si, ester and phosphate. Cracking in pellistor occurs when methane percentage is more than 5% which causes permanent damage of the bead. Lifetime of this sensor is also very short, maximum up to 2 years. Frequent failures occur in the system and it is very difficult to replace the sensor. It is understood that methane monitoring equipment worth crore of rupees is lying unused in different collieries in India, mainly due to lack of sensors. Therefore, it is of great interest to design and develop fiber optic methane sensor (FOMS) for mines, which would be intrinsically safe.

Several workers [9]–[15] have tried to exploit the attractive features of fiber optics in mines. Recently, the authors [16]–[19] have explored the idea of various

*This work is a review of the actual state of affairs in the relevant field.

possible applications of fiber optic sensors in underground coal mine as well as in geophysics. In this paper, a brief description of various types of fiber optic methane sensors is provided, with special emphasis towards their suitability to underground coal mines.

Coal is a porous substance having porosity between 2–14%. These pores are of two types: macropores and micropores. The size of micropores ranges between 5–20 Å. The methane molecules, where the C–H bond length is 2.4 Å, lie in these micropores. Further, the CH_4 molecule is a spherical top, belonging to the tetrahedral point group in a rigid rotor approximation [20]. It has four fundamental vibration frequencies: $\nu_1 = 2913.0\ cm^{-1}$, $\nu_2 = 1533.3\ cm^{-1}$, $\nu_3 = 3018.9\ cm^{-1}$ and $\nu_4 = 1305.9\ cm^{-1}$ [21]. In the near-infrared region (NIR), many overtone and combination bands arise. One of them, the combination band of $(\nu_2 + 2\nu_3)$ around 1.33 μm, was first measured by NORRIS and UNGER in 1933 [22], and after a long gap by CHAN *et al.* in 1983, who observed it at 1.3312 μm. Another overtone of CH_4 has been observed at 1.666 μm due to $2\nu_3$ band [24].

Different researchers [25]–[30] have used the absorbance in the optical power at these wavelengths and some other wavelengths [18] such as 2.25, 3.33, 3.39, and 7.7 μm for the detection of CH_4 gas using the different methods. These methods are discussed in the following sections.

2. Optical absorption (OA) method [31]–[40] of detection of CH_4 gas in NIR region

The application of an optical fiber link to the optical absorption cell was first proposed by INABA *et al.* [31] using low-loss fibers. Figure 1 depicts schematically the block diagram of an optical system for remote detection of CH_4 gas based on OA method. The pulsed light from LED is guided along the optical fiber to the remote gas sensor cell. Collimated light is passed through the sensing volume, where it

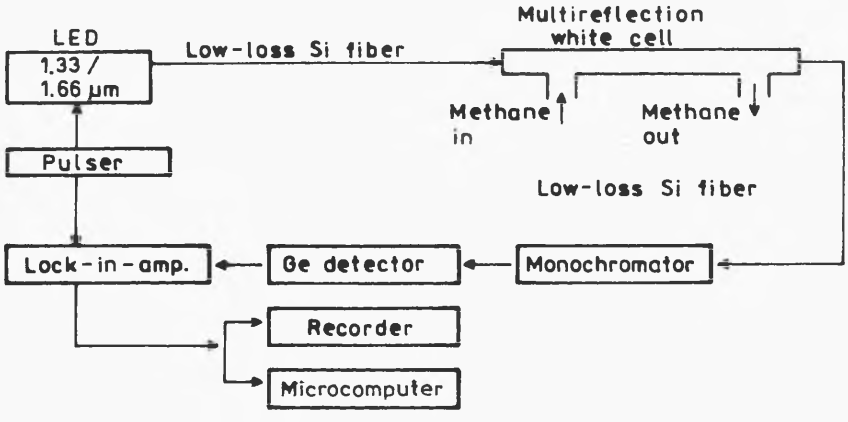

Fig. 1. Block diagram of an optical system for remote detection of CH_4 gas based on optical absorption method

it is selectively attenuated by any methane present. It is then refocused into the return fiber which guides it to detector through monochromator, lock-in-amplifier and finally to recorder or micro-computer. INABA [32] used an InGaAsP LED of 1.33 μm wavelength, multimode fibers of 50/125 μm core-clad diameter, transmission loss of nearly 1 dB/km, length 1 km+1 km and cell length 0.5 m, detected up to 1000 ppm of CH_4 or 1/50 of lower explosive limit (LEL) being confirmed with resolution of 0.3 nm. Recently, NAGAI *et al.* [33] have demonstrated a long distance remote sensing of methane gas using a 1.65 μm LD and a single mode fiber.

In addition to CH_4, other polluting gases such as propane, ethylene, butane, ethane and ammonia have also been detected using this method. These have been described elsewhere [34]–[43].

3. Differential optical absorption (DOA) method of detection of CH_4 gas [32], [39], [41], [44]–[46]

The block diagram of differential optical absorption method for the detection of CH_4 gas is shown in Fig. 2. In this method, light absorption is based on two optical wavelength bands. The measurement is basically implemented by employing a laser source located at the control center, from where an optical fiber is connected to a multireflection white cell [47] with multi-pass geometry, placed at a remote point to be monitored. ZIENTKIEWICZ [13] has used a tight steel tube approximately 1 m long and 10 cm in diameter, having gas inlet and outlet pipes as sample cell instead of white cell for detecting CH_4 in an underground mine. If extremely low-loss optical fiber is available in the frequency range concerned, a conventional nonlaser source such as LED and a multiple-wavelength discharge tube could also be utilised

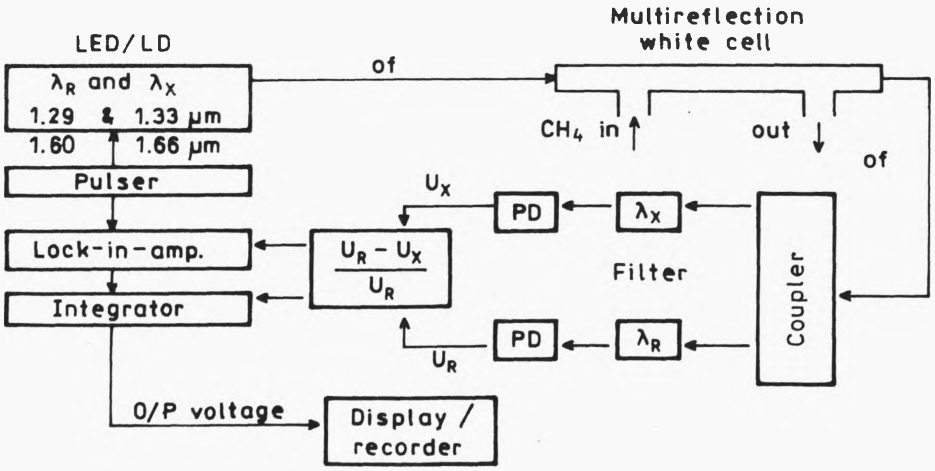

Fig. 2. Block diagram of an optical system for remote detection of CH_4 gas based on differential optical absorption method

in place of LD which can be tuned to or coincide with two frequencies λ_X and λ_R, in which at least one frequency is in absorption region of CH_4 gas, *i.e.*, 1.33 or 1.66 μm and another is at an adjacent reference wavelength, say, $\lambda_R = 1.29$ μm or 1.60 μm. Both optical signals are passed through the sample cell and returned to a coupler.

The light from one part of the coupler is passed through a bandpass filter with the spectrum centered at 1.29 μm. The output of the filter serves as the reference signal and is used to monitor variation in power output of either LED or the light launched into the filter. The light from the other port of the coupler passes through a bandpass filter with its spectrum centered at 1.33 μm, which corresponds to the absorption peak of methane.

The output light level from the reference and the sensor ports is linearly converted into electrical signals with low noise photodiodes and a high impedance amplifier and subsequently is measured with a lock-in-amplifier. The presence of methane in the sensing volume results in a dip in the transmission. The magnitude of the dip is proportional to the concentration of methane.

MOHEBATI and KING [45] have used diode lasers acting as both the light source and the wavelength selection device to eliminate the drift and noise of DOA fiber optic gas sensor. They have used two different diode lasers of widely different wavelengths of 0.8 μm and 1.33 μm and measured differential absorption using etalon to scan two modes of a diode laser. Recently, JIN *et al.* [46] have shown the performance limitation of fiber optic methane sensor due to interfacing effect.

4. Infrared fiber optics method of detection of CH_4 gas [48], [49]

The availability of zirconium fluoride (ZrF), [48], and chalcogenide IR transmitting fibers makes possible the detection of CH_4 gas with absorption bands in NIR region. ZrF fibers can transmit 2 – 5 μm region with attenuation of 10 – 40 dB/km. MATSON and GRIFFIN [49] have used ZrF IR fiber with core/clad diameter of 250/330 μm, NA = 0.21, loss $\leqslant$ 20 dB/km, transmission range 0.3 – 4.5 μm, minimum bend radius 11 mm with protective coating of epoxy acrylate of 45 μm thickness for detecting hydrocarbons. Based on IR transmitting fiber, MATSON and GRIFFIN [49] have suggested three types of gas sensor cells: (i) a simple vapour absorption cell, (ii) a photoacoustic cell, and (iii) an expensive FTIR interface to a remote gas analysis cell. Only the first one is described here. Figure 3**a** shows a conceptual block diagram of the IR fiber optic vapour absorption cell sensor probe. The probe consists of a duplex IR fiber cable terminated in a single tandem connector, a rigidly mounted collimating lens, gas ports, and an adjustable mirror. Figure 3**b** shows the block diagram of IR fiber optic vapour absorption sensor evaluation set-up. A typical design is a cylindrical tube with IR transmitting window at both ends. For the laboratory set-up, MATSON and GRIFFIN [49] have used a commerical FTIR spectrometer gas cell (10 cm long) as a probe. The ends of the cell were closed-off by CaF_2 windows (2 mm thick). Light from 3.39 μm He-Ne laser driven by the IR fiber was collimated into 1.0 inch diameter beam by a 2.5 inch focal length ZnSe lens. By adjusting the mirror, the light can be coupled into the second, or output, fiber

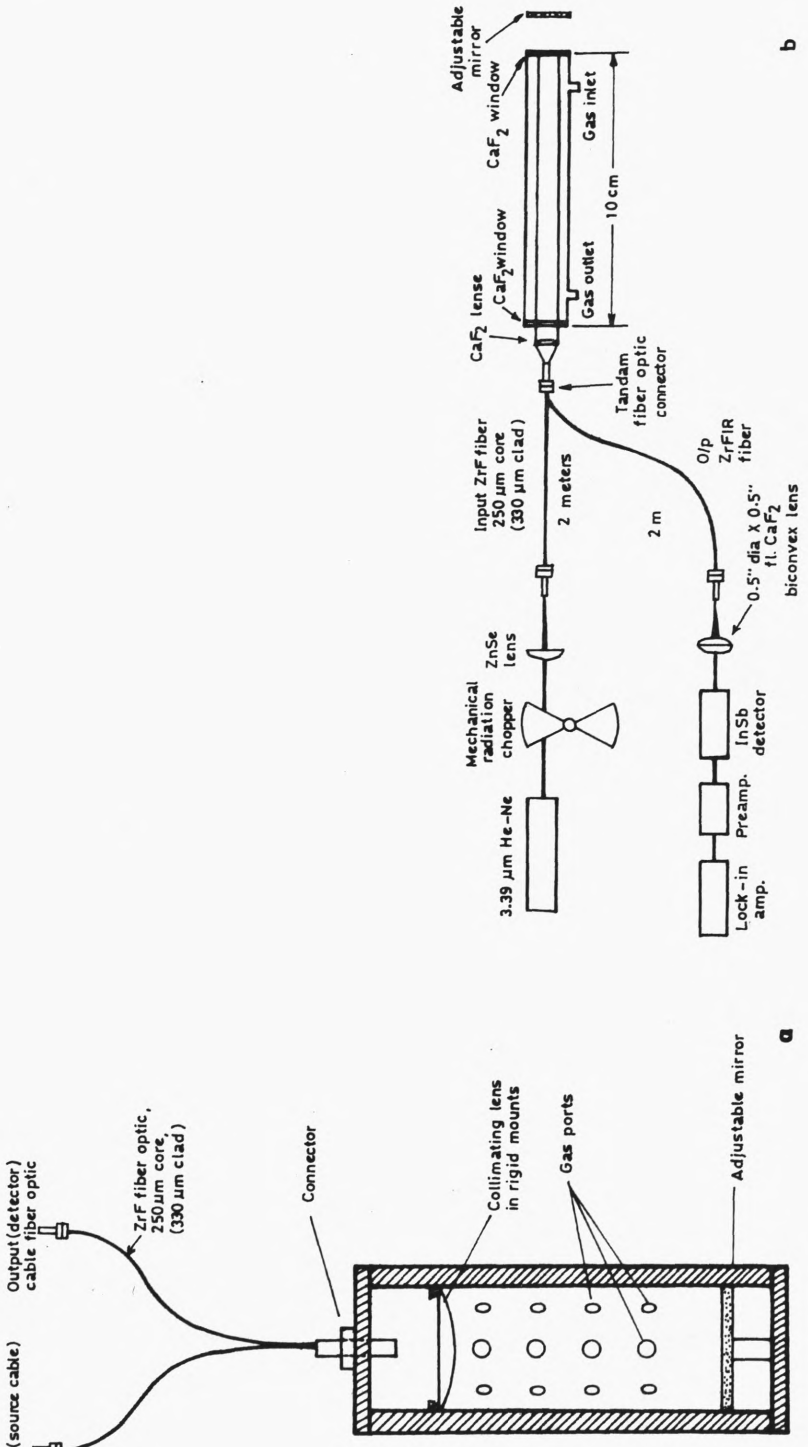

Fig. 3. Conceptual diagram of IR fiber optic absorption cell probe (a). Block diagram of IR fiber optic vapour absorption sensor evaluation set-up (b)

in the tandem connector. At the end of the output fiber, a cooled InSb detector captures light and modulates at the source frequency. Signals from detector are fed into a lock-in-amplifier finally calibrated for the hexane and minimum detection limit which was found to be 0.01%.

5. Evanescent wave spectroscopy method of detection of CH_4 [48], [50]

It has been observed that the amplitude of the field in cladding decays exponentially and is referred to as an evanescent field. There are several types of IR absorption sensors based on evanescent field device. This device is commonly used for analysing liquid phase samples in commercial FTIR spectrophotometers. Recently [48], [50], the following three types of probes have been proposed using fluoride fiber for the detection of methane and propane gases using the source within 3.2 – 3.6 μm region:

a) In the first one, a short section of cladding is removed from multimode fiber to access the evanescent field region.

b) In the second, the gas diffuses through the pores of sol-gel or teflon cladding of fiber causing an attenuation of the evanescent field and thereby a reduction in transmittance of the fiber.

c) In the third, an evanescent wave methane detection has been suggested using D-fiber or cladding reduced locally by polishing.

These are briefly described in the following sections.

5.1. Cladding removal with evanescent wave modulation [42], [51]

In this method, a cylindrical or planar optical waveguide is used and its construction is such that a part of the guided electromagnetic field extends beyond the physical boundary of the waveguide, as shown in Fig. 4a. An attenuation of this field can be

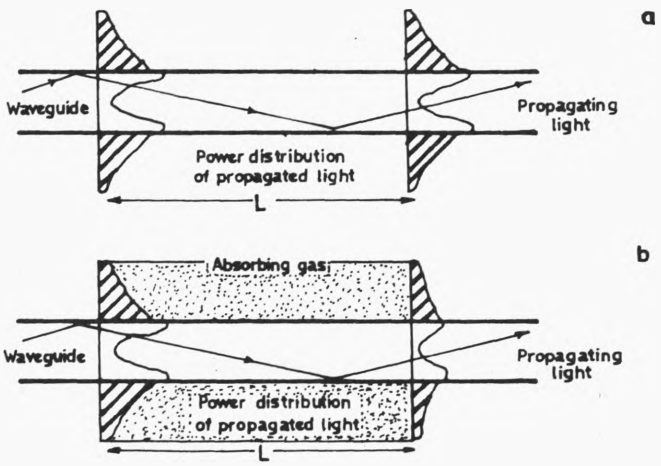

Fig. 4. Principle of detection of absorbing substance using an evanescent field. The power distribution of the propagated light through a waveguide is shown (a). When an absorbing substance, gas or liquid, surrounds the waveguide (b)

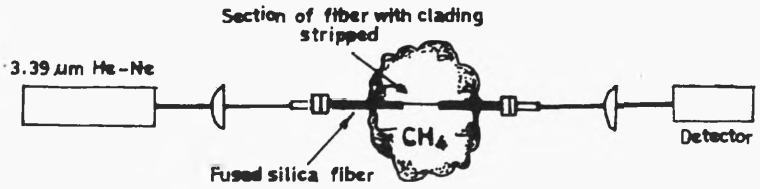

Fig. 5. Device for the detection of methane based on the attenuation of the evanescent field

observed when an absorbing substance is present at the waveguide boundary, as shown in Fig. 4b. Any phenomenon that disturbs the intensity of the evanescent wave also produces modulation in the intensity of the fiber-guided light. A cylindrical waveguide and a 3.39 μm He-Ne laser have been used by TAI *et al.* [51] for detection of CH_4 in nitrogen. In this experiment, a 40 cm long fused silica fiber served as waveguide. Several millimeter section of the fiber was stripped of its cladding to allow the evanescent field to penetrate into the ambient air. A representative diagram of this system is shown in Fig. 5. The authors of [42], [51] were able to detect CH_4 concentration down to 5% with this system.

5.2. Sol-gel cladding [42], [52], [53]

A layer of sol-gel makes an extremely versatile callding, as shown in Figure 6. The sol-gel process is the same as that used in making glass and ceramics at low temperatures via hydrolysis and polymerization of organic precursors. A combination of metal alkoxides, solvent, catalyst and water are mixed to obtain homogeneity. The hydrolysis and condensation polymerization produce a viscous gel, which is an amorphous porous material containing liquid solvent in its pores. The gel is heated at less than 100 °C so that most of the liquid is expelled, leaving the porous oxide, and then densified at a higher temperature. The materials and their concentrations can be modified to vary both the material's refractive index and porosity. This process is especially suited to produce a thin layer deposited on the fiber core. An uncladded fiber covered by a layer of sol-gel can either be used directly or else a reagent with absorption or fluorescence varying with an external parameter can be trapped in the sol-gel.

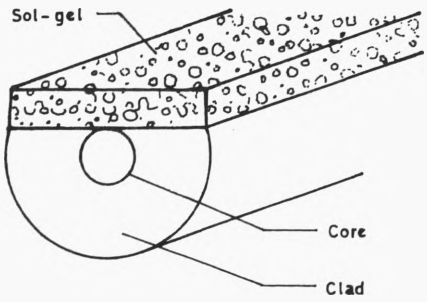

Fig. 6. Sol-gel coating for fiber optic intrinsic sensing

Cladding with colour variations [53] has also been used for detection of hydrocarbons. In this technique the colour, and thus absorption spectrum of the cladding can be modulated by an external parameter.

5.2. Evanescent field detection of CH_4 gas using D-fiber [50], [51], [54]–[56]

D-fibers are produced by polishing a flat on the fiber preform to give a D-shaped cross-section, and then preform is subsequently pulled into the fiber. D-fiber may be used as evanescent wave CH_4 gas sensor by performing attenuation measurements on guided wave at a wavelength corresponding to 1.33 and 1.66 μm. Figure 7 [50]

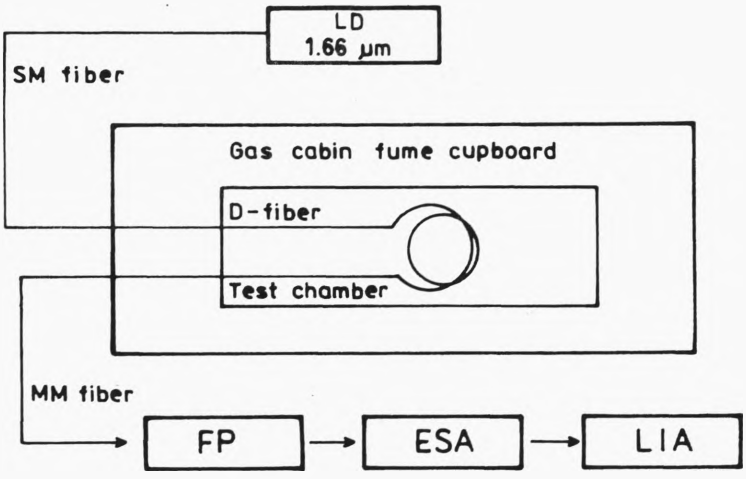

Fig. 7. Block diagram for detection of methane gas using D-fiber

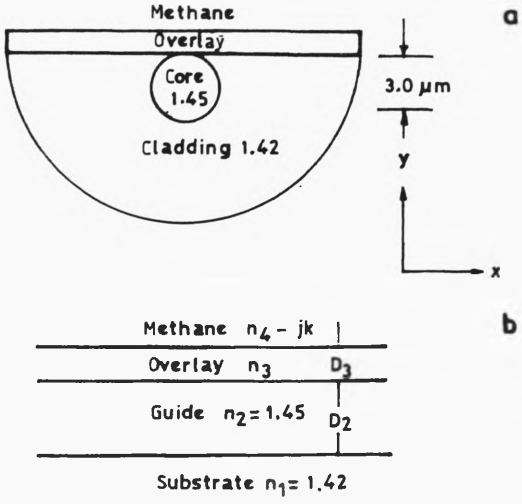

Fig. 8. Cross-section of overcoated D-fiber used for methane detection (not to the scale), (a). Overcoated planar waveguide with thin high index overlay (not to the scale), (b)

shows the block diagram of a CH_4 gas sensor using D-fiber. In this set-up a LD of 1.66 μm was coupled into a length of standard single-mode (SM) fiber spliced on to a 5 m length of D-fiber, core diameter of 3 μm and zero *d*-distance [54], [55]. The D-fiber section has been inserted into the methane gas test chamber and output of the D-fiber has been connected to a scanning Fabry–Perot (FP) resonator by a length of a multimode (MM) fiber. The detected signal from the FP could be monitored with an electronic spectrum analyser (ESA). The sensitivity of D-fiber was compared with that of an open path gas cell using the same detection system. Per equal length, the D-fiber was found to be less sensitive, which can be improved by increasing index difference Δn (*e.g.*, increasing Δn from 0.02 to 0.03, sensitivity increased twice). It has been shown by MUHAMMAD *et al.* [54] that the sensitivity of D-fiber methane gas sensor can be realistically improved by overcoating the flat surface of fiber with a high index layer. Cross-section of overcoated D-fiber is shown in Figs. 8**a**,**b**.

6. Correlation spectroscopy for the detection of CH_4 gas [57]

Recently, DAKIN and EDWARDS [57] have reported gas sensor using real-time correlation spectroscopy, where a gas is used as a matched optical fiber to recognize its own spectral absorption lines. The basic concept of correlation spectrometry involves the passage of light sequentially through two gas cells: a reference cell containing a known quantity of the gas to be detected, and a sampling cell where the presence of the gas is to be determined. An optical signal passing through both cells will suffer absorption due to the presence of gas in each. If the absorption in the reference cell is periodically modulated, then the total absorption depends on whether the gas absorption lines in the sampling cell correlate with those in the reference cell gas. It is similar to the optical methanometer presently being used for the detection of methane.

7. Discussion

The optical detection of methane gas by OA and DOA methods requires an open cell with light propagating through it as the detection system. This requires a precise, expensive and delicate alignment of optics. Further, it has disadvantage of transmitting the light to NIR region, so that only the weaker overtone bands can be monitored. On the other hand, the low-loss fiber (1 dB/km) has the advantage of transmitting the light to a longer distance, which allows the sensor head to be sited remotely from the monitoring station, and offers the possibility of multiplexing a number of sensors. Thus, the OA and DOA methods of detection of methane gas may not be very much suitable for the underground mines.

In the case of fluoride fiber, there is no restriction to transmitting the light of NIR region only, it can transmit the wavelength between 2–5 μm or more, which helps us in detecting the main absorption band of methane gas at 2.27, 3.33 and 3.39 μm but the IR fibers are having more loss (20 db/km), and hence cannot be used for remotely

located gas cell at a long distance in underground mines. These fibers are expensive and hygroscopic, and hence may not be much suitable for the underground mines where the environment is humid in addition to being explosive and toxic. The IR fiber optic methane sensors are good for few meters measurements or in fiber optic instruments. Recently [49], [58], a fiber optic FTIR instrument was made available that can support 100 m ZrF fiber and a gas cell. However, the price of the fiber optic FTIR is more than $ 70,000. This appears very expensive for mining application. Correlation spectroscopy may not be suitable because it requires a gas filled cell for the reference, which may leak after certain time.

An evanescent field device has the advantage that it can be both optically and mechanically coupled directly to an IR fiber optic link, which makes rugged and low-light loss package. The absorption characteristics of D-fiber obviate the entire precision optics when used for methane detection. From the above discussion it follows that the evanescent field detection of CH_4 gas using D-fiber may be best for the mining purposes. It is more rugged having less expensive optics and may be used for a long-distance network.

Parallel and sequential measurements [40] can be made employing a number of pairs of optical fibers connected to the individual sample cell kept at different locations in underground mines for the monitoring of CO and CH_4 gases, and useful information regarding their concentration can be obtained. Using OTDR, a distributed gas sensor system can be designed specially for the underground coal mines. A laboratory model for fiber optic methane sensor is under development and will appear in the forthcoming paper.

One of the major advantages of the optical gas detection system is that it is intrinsically safe, flameproof and fail-safe. It will not give a misleading zero reading if CH_4 gas is in dangerous limit. A catalytic type detector may not detect CH_4 gas at all if catalyst has been contaminated.

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